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Study on modification of ternary carbonates with additives

L. X. Sang,* M. Cai, N. Ren, Y.T. Wu

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education and Key Laboratory of Heat Transfer and Energy Conversion, Beijing Municipality, College of Environmental and Energy Engineering,Beijing University of Technology, Beijing, 100124, China.

Abstract

In order to improve the thermal physical properties of ternary carbonates, potassium, lithium, and sodium carbonates were modified by adding additives CaO, $CaCO_3$, $Ca(OH)_2$ and KOH. Their melting point, initial crystallization point, and decomposition temperature were analyzed by using the Synchronous Thermal Analyzer. Although the additives have less influence on the initial crystallization temperatures and the decomposition temperatures of ternary carbonates, they have different effects on the melting point of ternary carbonates. For concentrating solar power, KOH could be a good candidate of practical additive to expand the work temperature range of ternary carbonates by reducing melting point in a great extent.

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Key*words:* ternary carbonates, additive, melting point, intial crystallization point, decomposition temperature.

1. Introduction

Concentrating solar power (CSP) is a large-scale, commercially available way to make electricity by using solar energy [1]. Solar heat transfer and heat storage technology is the key to the CSP system because the CSP system needs to maintain normal operation by relying on stored energy at the times of lesser irradiation in the mornings, evenings or during cloudy weather days [2,3]. Heat storage for solar thermal power plants also can be helpful to reduce the electricity generation cost due to increased solar's share, more operating hours per year, and less part-load operation [1,4]. Molten salts have been considered as a good choice of heat storage medium for CSP system energy

* Corresponding author. Tel.: +86-010-67391612-8317; Fax: +86-010-67392774.
E-mail address: sanglixia@bjut.edu.cn

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storage and transportation in view of their wide work temperature range, large heat capacity, low cost, good chemical stability[5,6]. So far, several available mixed molten salts composed of nitrates and nitrites have been used for CPS systems[7-9]. Among of them, Solar Salt, the binary nitrates ($NaNO_3$:KNO_3=60:40,wt%), melts at 220 ℃ and decomposes at 600 ℃ [10,11]. Hitec, the ternary molten salts ($NaNO_3$:KNO_3:$NaNO_2$=7:53:40,wt%), and Hitec XL($NaNO_3$:KNO_3:$Ca(NO_3)_2$=7:45:48,wt%) are developed as both commercial mixed molten salts[12-14]. Their melting point and the decomposition temperature are lower than that of Solar Salt. Compared with nitrates, the mixed carbonates can meet the requirements of high temperature solar thermal power generation [15,18]. The decomposition temperatures of mixed carbonates can be up to 1000 ℃, [19]. Our research group (B.J.U.T.) [20,21]have investigated in details the thermophysical properties of ternary carbonates and found that the melting point of the ternary carbonates with optimized composition can be as low as 400 ℃, and the decomposition temperature were maintained 800 ℃, and above. In the present work, in order to further reduce the melting point and widen the work temperature range of carbonates, the additives, CaO, $CaCO_3$, $Ca(OH)_2$, KOH, were added into the ternary carbonates. The melting points, initial crystallization points, decomposition temperatures of the prepared mixed molten salts were determined.

2. Experimental

The materials used in the presented experiments were lithium carbonate, sodium carbonate, potassium carbonate, potassium hydroxide, calcium hydroxide, calcium carbonate and calcium oxide. All carbonates and hydroxides were anhydrous and analytical reagent grade chemicals. The mixed molten salts were prepared through the direct mixing preparation method [17] according to mass ratio or molar ratio shown in Table 1. During the preparation, the raw materials were dried at 150℃ for 24 h, which can help to remove the crystal water in materials as fully as possible.

Table 1. Mass ratio of the mixed molten salts.

Samples	Mass ratio
TC(ternary carbonates)	K_2CO_3:Li_2CO_3:Na_2CO_3 =4:4:2
TC-CaO	K_2CO_3:Li_2CO_3:Na_2CO_3: CaO=4:4:2:1
TC-$CaCO_3$	K_2CO_3:Li_2CO_3:Na_2CO_3: $CaCO_3$-=4:4:2:1
TC-$Ca(OH)_2$	K_2CO_3:Li_2CO_3:Na_2CO_3: $Ca(OH)_2$=4:4:2:1
TC-KOH	K_2CO_3:Li_2CO_3:Na_2CO_3: KOH=4:4:2:1

Melting point, initial crystallization point, and decomposition temperature were analyzed with differential scanning calorimetry (DSC). Simultaneous Thermal Analyzers (STA-409PC, NETZSCH) were used to obtain the DSC curves from 20 ℃ to 1500℃ with a maximum working temperature of 1500 ℃ and a weighing precision of 0.001 mg. The precision of the experimental apparatus was validated by measuring DSC with industrial-grade lithium nitrate in platinum–rhodium (Pt–Rh) crucibles. The error between measured values and the literature value on the melting point was 1.6 % [20].

3. Results and discussions

3.1 Melting point

The heating curves show the mixed molten salt's melting process, as shown in Fig.1. If the mixed molten salts can form eutectics, it can be found that they have typical melting peaks. The melting temperature ranges of the mixed molten salts with typical melting peaks are narrow, around 10℃, which is appropriate and displays that the salts can melt in a relatively short range of temperature and period of time. Through analyzing every heating curve individually, there is the irregular melting peak instead of typical melting peak to be appeared in ternary carbonates with $Ca(OH)_2$ (Fig. 1d). Although ternary carbonates with $CaCO_3$ has typical melting peak(Fig 1c), compared to TC' melting point of 410.5℃(Fig 1a), the melting point of the mixed molten salts can't be reduced. That is, it is difficult to lower the melting point of ternary carbonate by adding calcium carbonate. When adding CaO into the

ternary carbonates (Fig. 1b), the melting point can be lowered, but the melting temperature range is relatively large, which is not appropriate to be used in CSP. As for additive KOH, typical melting peak can be formed after the first heating and cooling cycle experiment. Particularly, the melting point of ternary carbonates with KOH is 321.5℃(Fig. 1e). The difference of the melting point between TC and TC-KOH is up to 89℃. Thus, the temperature range of the liquid phase can be widen, which can reduce the risk of frozen slat blocks in the pipes.

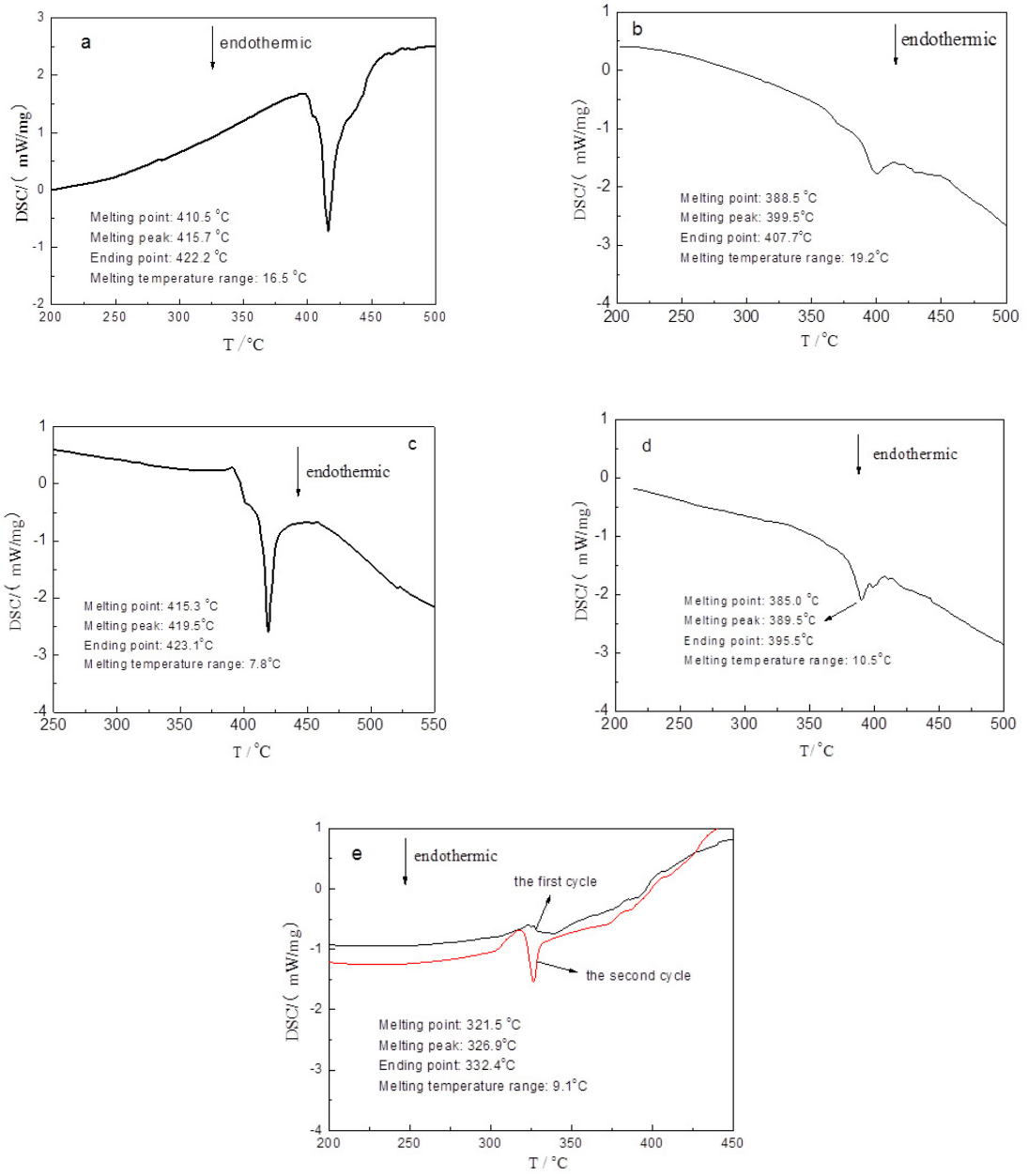

Fig. 1. DSC heating curves of ternary carbonates(a) and ternary carbonates with CaO(b) , $CaCO_3$(c), $Ca(OH)_2$(d), and KOH(e)

3.2 The initial crystallization point

The initial crystallization point of the mixed molten salts can be obtained by analyzing their DSC cooling curves. Shown in Fig. 2, it can be known that the initial crystallization point of the ternary carbonates is 384.2 ℃. Table 2 shows the initial crystallization points of the ternary carbonates with and without additives. Except for sample TC-$Ca(OH)_2$, the ternary carbonates with CaO and KOH have relatively lower initial crystallization temperatures, which is lower than that of the corresponding ternary carbonates. Although the difference of the initial crystallization point is small, it is helpful to avoid an imminant risk of frozen blocks in pipes when using ternary carbonates with KOH or CaO.

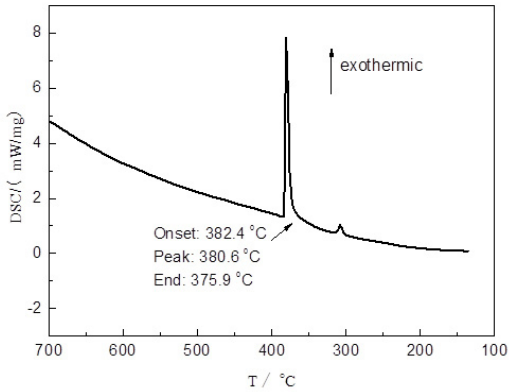

Fig. 2. DSC cooling curve of ternary carbonates for obtaining the initial crystalization point

Table 2. The initial crystallization point of the mixed molten salts.

Samples	The initial crystallization point/ ℃
TC(ternary carbonates)	382.4
TC-CaO	377.7
TC-Ca(OH)2	386.3
TC-KOH	375.6

3.3 The decomposition temperature.

The decomposition temperatures of the new mixed salts can be determined by TG curves, as shown in Fig. 3. From Fig. 3, all of them begin to decompose and their mass decrease rapidly at the temperature range of 800-900 ^{o}C. The decomposition temperature of TC-CaO, TC-$Ca(OH)_2$ or TC-KOH is 884, 836, and 865^{o}C, respectively, which indicates that these additives had a little influence on the decomposition temperature of the ternary carbonates(850^{o}C). A higher decomposition temperature can raise the maximum work temperature of CSP, which also is beneficial to develop supercritical and ultra-supercritical power generators.

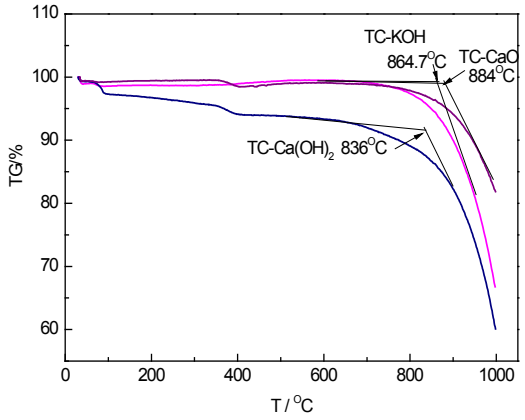

Fig. 3. TG curves of ternary carbonates with CaO, $Ca(OH)_2$, and KOH

4. Conclusion

Four kinds of the mixed molten salts were prepared by adding different additives CaO, $CaCO_3$, $Ca(OH)_2$, and KOH to the ternary carbonates with mass ratio (K_2CO_3:Li_2CO_3:Na_2CO_3=4:4:2). The melting point, initial crystallization point and decomposition temperature were tested and analyzed by using synchronous thermal analyzer.

Adding $CaCO_3$ is failing to lower the melting point of ternary carbonate. CaO and $Ca(OH)_2$ can't be good candidate of practical additive due to irregular melting peak and the larger melting temperature range. The additive KOH has more significant effect on lowering the melting point of ternary carbonate mixtures, the reduced value can be up to 89 °C. When choosing CaO, $Ca(OH)_2$, and KOH as additive, the initial crystallization points of the mixed molten salts are lower than that of the corresponding ternary carbonates, and the decomposition temperatures can be maintained at above 800 °C. Although KOH could be a good candidate of practical additive for ternary carbonates, their cost comparsion, corrosion performance and long-term stabiltity need to be further studied.

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